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厦门大学

博　士　学　位　论　文

Co-X (X: V, Ta)基合金热力学数据库的建立及其合金设计

Development of thermodynamic database of Co-X (X: V, Ta) base alloys and its applications in alloy design

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摘要

Co 基合金具有良好的磁学性能、耐磨性、耐热性、耐腐蚀性以及生物相容性，因此在国防和民用工业中是一种重要的金属材料。然而长期以来对新型 Co 基材料的开发通常是凭借经验或是采用试错法，缺乏相应的理论指导，研发周期长，耗资大，效率低。近年来，随着“材料基因组”计划的提出，研究者希望能够重组 Co 基材料的“材料基因”，从而可以根据工业需求来有目的地研发新型 Co 基材料。CALPHAD (CALculation of PHAse Diagram)是一种行之有效地获得“材料基因”的方法，基于热力学数据库可以对材料的组织和性能作出预测。目前，专业的钢铁合金、镍基高温合金、铝合金、镁合金、铜合金以及无铅焊接材料热力学数据库均已经被开发并商业化，但还没有一个比较完善的 Co 基合金的热力学数据库。因此，建立关键应用领域 Co 基合金(包括 Co 基高温合金、垂直磁记录材料等)的热力学数据库，无论是对于 Co 基新材料的开发还是对目前已有 Co 基材料的性能改进，都具有重要的理论价值和实际意义。

本研究通过合金法和扩散偶法对部分重要的 Co-X (X: V, Ta)基合金体系的相图进行了实验研究、结合部分已报道的热力学性质及相平衡信息，采用 CALPHAD 方法，对部分重要的 Co 基二元和三元系相图进行了热力学优化与计算，获得了自洽性良好的热力学参数。基于获得的热力学参数，计算的相图与实验相图符合较好。此外，本研究以 Co-V 基磁性薄膜的设计及制备为例，介绍了数据库在材料设计上的应用，研究结果表明该数据库可以为 Co 基材料的研发提供重要的理论指导。以下为本研究的主要内容：

(1) 通过合金法或扩散偶法，采用 EPMA 背散射电子图像组织观察、WDX 成分分析以及 XRD 相结构分析等方法，对 Co-V 二元系、Co-V-Cr (800℃、1000℃、1100℃、1200℃)、Co-V-Fe (800℃、1000℃、1100℃、1200℃)、Co-V-Ni (800℃、900℃、1000℃、1100℃、1200℃)、Co-Ta-Cr (800℃、900℃、1100℃)、Co-Ta-Ni (1200℃、1300℃)、Co-Ta-Fe (1000℃)以及 Fe-Ni-V (1000℃、1100℃、1200℃)共计 8 个合金体系进行了相平衡的实验测定，获得了共计 22 个等温截面相图。研究结果表明：σ相在 Co-V-X (X: Cr, Fe, Ni)各三元系中均形成了连续固溶体(化

合物)相；在 Co-Ta-Cr 三元系中，高温相$(Co, Cr)_2Ta$(HT)相在低温段会被稳定化；本研究测定的全部等温截面相图中均未发现三元化合物相。

(2) 结合本研究所获得的实验结果和文献报道的实验信息，采用 CALPHAD 方法，对 Co-V 二元系相图进行了热力学优化与再计算。为了统一热力学模型，对 Co-Ta、Fe-Ta 及 Ni-Ta 各二元系相图进行了热力学再计算。在本研究及文献报道的实验信息的基础上，对 Co-V-X (X: Cr, Fe, Ni)、Co-Ta-X (X:Cr, Fe, Ni)以及 Fe-Ni-V、Co-Fe-Ni 和 Cr-Fe-V 各三元系相图进行了热力学优化与计算，并建立了 Co-X (X: V, Ta)基合金的热力学数据库。

(3) 基于本研究建立的 Co-X (X: V, Ta)基合金的热力学数据库，对 Co-V 二元及 Co-V 基三元系的 hcp 两相分离的相界线(亦称溶解度间隙)进行了热力学计算，并分别计算了铁磁性 hcp 相与顺磁性 hcp 相的相分数随成分及温度的变化曲线。在计算结果的基础上，设计了 Co-V 二元及 Co-V-Ta 三元合金薄膜的成分，并利用磁控溅射法制备了一系列 Co-V 基合金薄膜，对其微观组织和磁学性能进行了研究。研究结果表明：Co-V 二元系中存在亚稳的 hcp 两相分离；Co-V 基合金薄膜的微观组织及磁学性能与计算结果之间存在较好的对应关系；相图计算对 Co-V 基磁垂直记录材料的设计起到了重要的指导作用。

关键词：Co 基合金；CALPHAD；相图；薄膜

# Abstract

The cobalt-based alloys play an important role in the defense and civilian industries because they exhibit excellent magnetic properties, wear resistance, heat resistance, corrosion resistance and biocompatibility. In the past decades, the developments of the Co-based alloys were always based on empirical methods or trial-and-error due to the lack of the theories, resulting in a great waste of time and money. In recent years, with the proposal of “Materials Genome Initiative”, researchers expect to purposefully develop new Co-based alloys by rebuilding the “materials genome” of Co-based alloys. CALPHAD (CALculation of PHAse Diagram) is an effective method to find the “materials genome”, by which some properties of materials could be predicted based on the thermodynamic database. To date, the thermodynamic databases of steels and Fe-, Ni-, Al-, Mg-, Si-, Cu-based alloys and lead-free soldering materials are commercial, but a systematic thermodynamic database of the Co-based alloys is unavailable. Thus, the foundation of the thermodynamic database of the Co-based alloys is important for the development of the Co-based materials.

In the present work, phase equilibria of some important Co-X (X: V, Ta) base alloy systems were experimentally investigated by using equilibrated alloys and diffusion couples. Based on the experimental data from this work and literatures, some important Co-based systems were thermodynamically assessed by using CALPHAD method. Good agreements are obtained between the calculated results and experimental data. The application on the material design of the thermodynamic database was presented by the design of the Co-V base magnetic recording thin films. The microstructure and magnetic properties of the prepared thin films were investigated. The obtained thermodynamic database may provide useful information for the development of the Co-based alloys. The main contents of this work are listed as follows:

(1) The phase equilibria in the Co-V binary system, Co-V-Cr (800℃, 1000℃,

1100℃, 1200℃), Co-V-Fe (800℃, 1000℃, 1100℃, 1200℃), Co-V-Ni (800℃、900℃, 1000℃, 1100℃, 1200℃)、Co-Ta-Cr (800℃, 900℃, 1100℃), Co-Ta-Ni (1200℃, 1300℃), Co-Ta-Fe (1000℃) and Fe-Ni-V (1000℃, 1100℃, 1200℃) ternary systems were experimentally researched by BSE images, WDX and XRD analysis. 22 isothermal sections were obtained. The experimental results show that the σ phase forms continuous solid solution in Co-V-X (X: Cr, Fe, Ni) ternary systems, the high-temperature phase (Co, Cr)$_2$Ta(HT) becomes stable at low temperature in the Co-Cr-Ta ternary system, no ternary compound was found in present work.

(2) Based on the experimental data of present work and literatures, the Co-V binary diagram was thermodynamically calculated by using CALPHAD method. The Co-Ta, Fe-Ta and Ni-Ta binary diagrams were recalculated to build compatible thermodynamic models. Co-V-X (X: Cr, Fe, Ni), Co-Ta-X (X:Cr, Fe, Ni), Fe-Ni-V, Co-Fe-Ni and Cr-Fe-V alloy systems were thermodynamically calculated. The thermodynamic database of Co-X (X: V, Ta) base alloys was established based on the present work and previous works.

(3) Based on the thermodynamic database of Co-X (X: V, Ta) base alloys established in present work, the phase boundary lines of hcp phase separation (miscibility gaps) in the Co-V binary system and Co-V based ternary systems were calculated, the Co–V thin films with different components were deposited by magnetron sputtering. The microstructures and the magnetic properties of thin films were investigated. The experimental results show that the metastable phase separation in the hcp phase exists in the Co-V system, the microstructures and magnetic properties of the thin films consist with the calculated results very well, the CALPHAD method could be effectively used in the design of Co-V based perpendicular magnetic recording media.

Key words: Co-based alloys; CALPHAD; Phase diagram, thin films

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